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Reactions of Chlorine Dioxide and Other
Oxy-chloro Compounds with Organic Compounds

Supplement to
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Kinetics of Reaction Between Chlorine Dioxide and Phenol

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Introduction

The chlorination of water containing phenols may render it unpalatable. Chlorinated phenols in water have been rendered innocuous by the addition of chlorine dioxide.¹ The reactions between phenol or chlorinated phenols and chlorine dioxide was the objective of this research.

Paluche² reviewed the work of others on the reaction of chlorine dioxide on aromatic compounds including phenols. She concluded that chlorine dioxide can (i) break up the benzene ring to form oxalic, maleic, and fumaric acids and CO_2 , (ii) split the benzene ring at one location to form muconic acid and (iii) oxidize to form quinone. Furthermore, chlorine dioxide can form chlorine derivatives of the above mentioned products.

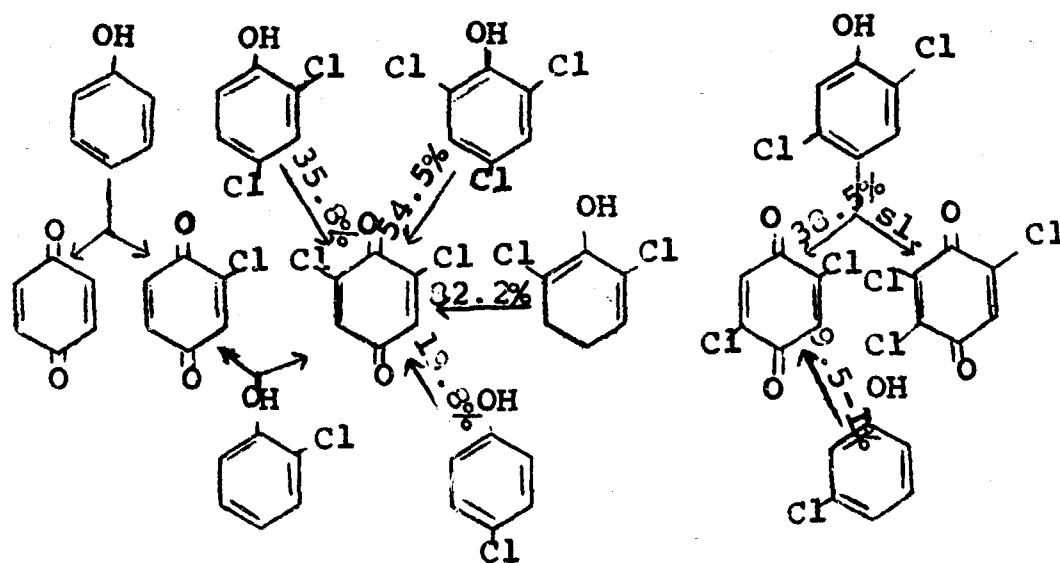
She reported on her own work which was the reaction of chlorine dioxide on phenols. The experiments were conducted by bubbling a chlorine dioxide-air gas mixture through an aqueous solution, emulsion or suspension, of the phenols. In all instances the reaction **resulted** in the formation of quinones, a small quantity of oxalic acid and some kind of tar substance not identified. The quantity in moles of oxalic acid produced per mole of phenol reacted is shown in Table 1.

Table 1

Quantity in Moles of Oxalic Acid per Mole of Acid Produced			
phenol	0.018	2,4 dichlorophenol	0.014
o-chlorophenol	0.032	2,5 dichlorophenol	0.018
m-chlorophenol	0.031	2,4,6 trichlorophenol	0.024
p-chlorophenol	0.052		

Also she presented the following diagram of Yield of quinones from the reaction of chlorine dioxide.

Table 2



In the second report Paluch³ described the results from reaction of chlorine dioxide with hydroquinones and nitrophenols. The experimental conditions were the same as in the previous work. The results of the reactions using chlorine dioxide are shown below. The yields of the derivatives are expressed as a percentage of the original hydroquinone or nitro phenol.

Table 3

hydroquinone	61.7%	p- benzoquinone
	→	
chlorohydroquinone	68.5%	chloro-p-benzoquinone
	→	
2,5 dichlorohydroquinone	79.2%	2,5 dichloro-p-benzoquinone
	→	
	86.6%	
2,6 dichlorohydroquinone	→	2,6 dichloro-p-benzoquinone
	97.6%	
tetrachlorohydroquinone	→	tetrachloro-p-benzoquinone
	8.4%	
p-nitrophenol	→	2,6 dichloro-p-benzoquinone
o-nitrophenol	→	oxalic + fumaric acids

There was some yield of oxalic acid and with the o-nitrophenol there was some fumaric acid.

It was the intent of the present research to make studies of a like nature in dilute aqueous solutions. These studies were to include analysis of reaction kinetics as well as identification of products. Only a part of the proposed studies were completed; the observation of reaction rates of chlorine dioxide with phenol at a single set of experimental conditions. The findings are reported below.

EXPERIMENTAL PROCEDURES

REAGENTS

Organic Free Distilled Water (O.F.D.)

The preparation of water suitable as a solvent for any of the oxychloro species was one of the most troublesome problems. The procedure adopted involved the redistillation of regular distilled water from acid permanganate (1% conc. H_2SO_4 and 1% KMnO_4), the permanganate being effective in removing volatile amines. The distillate traveled through a long vertical column containing glass beads and wrapped with asbestos. It was necessary to use a heating tape near the top of the column in order to break the continuous film of water from the distillation flask; otherwise, there was creeping of the permanganate and the distillate would contain about 10^{-5}M of the oxidizing agent.

Chlorine Dioxide (ClO_2)

Chlorine dioxide was prepared according to a method of Granstrom and Lee¹ by dissolving 4 grams of sodium chlorite in 50 ml distilled water in the reaction vessel--to this was added a solution of 2 grams of potassium persulfate in 100 ml distilled water. High purity nitrogen gas (Linde) was used to sweep out the chlorine dioxide formed; this $\text{N}_2 - \text{ClO}_2$ gas mixture was passed through a dry sodium chlorite column to remove any traces of hypochlorous acid which may have been formed; next, the gases were passed into a trap to remove any sodium chlorite dust which may have been carried over and finally the chlorine dioxide was collected in cool O.F.D. The temperature of the receiving solution was kept from 0-10°C, by immersing the container in a beaker of crushed ice; this increases the solubility of chlorine dioxide. A solution concentration which ranged from 2 to $10 \times 10^{-3}\text{M}$, could be prepared thus, the resulting concentration

being determined iodometrically at a pH of 1 to 1.5.

Buffer System

Previous experience showed us that a phosphate buffer system would be suitable for the studies under consideration since some of the ~~organic~~ buffer systems which could be used in this pH range (especially acetic ~~acid-acetate~~) may react with the oxychloro compounds present. In addition, the phosphate buffer system would hold the pH constant at a molal concentration of 0.1 or more under the experimental conditions anticipated in these studies. The ionic strength of the reaction was set at 0.3 and the evaluation of the ionic strength of the buffer systems has been previously described.

Initial studies were not done in buffered systems but only in aqueous solutions. Since the pH of these runs was in the vicinity of 4, subsequent runs were carried out in the phosphate buffer with the pH around 4.0(3.8 - 4.1).

Chlorine dioxide measurements were done in two ways--(a) spectral (b) iodometric titration. Spectral measurements were done at 357m μ using a molar absorptivity of 1242 to calculate the concentration. Iodometric titrations were done by adding excess KI and titrating the liberated iodine with sodium thiosulfate using starch as the indicator.

Phenol measurements were also done in two ways--(a) spectral (b) bromination. Spectral measurements were done at 270 m μ using a molar absorptivity of 1445 to calculate the concentration.

In the assay of phenol, bromine is employed as an oxidizing agent--it forms tribromo derivatives quantitatively that are insoluble in water in the presence of a slight excess of bromine. The volumetric solution does not contain bromine when treated with an acid--this bromine solution is known as Koppescharr's solution. It is prepared by dissolving 3 gms of potassium bromate and 15 gms of potassium bromide in sufficient water to make 1 liter. The normality is determined as follows: Measure 8 ml of the solution into a 500 ml iodine flask and dilute with 130 ml of water. Add 5 ml of concentrated hydrochloric acid, stopper the flask to prevent the escape of bromine vapors and shake it gently. Then add excess solid potassium iodide, re-stopper, shake the mixture and allow it to stand in the dark for 5 minutes. Titrate the liberated iodine with sodium thiosulfate, using starch as the indicator.

When the solution of potassium bromide and potassium bromate is acidified with hydrochloric acid, bromine is set free according to the reaction:

$5\text{KBr} + \text{KBrO}_3 + 6\text{HCl} \rightarrow 6\text{KCl} + 3\text{Br}_2 + 3\text{H}_2\text{O}$ and the liberated bromine oxidizes the iodide to iodine: $2\text{KI} + \text{Br}_2 \rightarrow 2\text{KBr} + \text{I}_2$.

In the analysis for phenol, an aliquot portion of the solution is transferred to a 500 ml iodine flask and mixed with the Koppescharr's solution. Concentrated hydrochloric acid is added and the flask is tightly stoppered to prevent the escape of the volatile bromine. The flask is shaken repeatedly during 30 minutes to mix the contents thoroughly and to allow the oxidation of phenol to tribromophenol to go to completion.

Allow the flask to stand for 15 minutes and then introduce quickly a quantity of solid potassium iodide, being careful that no bromine vapor escapes and re-stopper the flask at once. Shake the flask thoroughly, remove the stopper and rinse it and the neck of the flask with a little water so that the washings may flow into the flask. Then add 1 ml of chloroform to dissolve the precipitated tribromophenol, shake the mixture well and titrate the liberated iodine with sodium thiosulfate using starch as the indicator.

Making a Run

1. Separate stock solutions of chlorine dioxide and phenol were prepared and the concentrations determined iodometrically.
2. Aliquots of these stock solutions were taken to prepare each half sample and the buffer or buffer electrolyte was added.
3. Concentration of each half-sample was determined spectrophotometrically. In addition, the concentration of phenol was determined by the bromination procedure.
4. The phenol was placed in the reaction vessel and equal volume of chlorine dioxide added at time zero.
5. A portion of the reaction mixture was pipetted into the cuvette which was then put into the instrument. The blank cell contained all of the mixture components except the reactants.
6. The absorbance at 357m μ was read as a function of time.

Following the run spectra were taken of the product. Figure 1 is typical of the spectra of chlorine dioxide, phenal and reaction products. This product was possibly a mixture of quinines and chloroquinones but was not identified.

Results

Some 21 runs were made at an ionic strength of 0.3 molal and at a phosphate buffer concentration of 0.1 molal. The pH was nominally 4.0 with a range from 3.85 - 4.15. Because of interfering spectra, as shown on Figure 1, evaluation of the rate constant could be done only at time zero and at 357mμ, which is the wave length of maximum absorbance of chlorine dioxide. At this wave length the phenol does not absorb and at time zero no product has been formed. Thus, at this point only the rate of consumption of chlorine dioxide is being observed. Unfortunately establishing slopes at time zero is not always as accurate as desired because the first readings were not obtained in less than 20 seconds and sometimes more. Fortunately, initial absorbance readings on a portion of the reaction mixture were taken prior to mixing; so zero-time concentration readings were available. Smooth curves were drawn through the several points and a tangent was drawn by eye at time zero. Initial slope values were taken on each of the runs. A typical curve is shown on Figure 2.

It was assumed that the reaction between chlorine dioxide and phenol was second-order. The rate equation is expressed as Equation (1).

$$\frac{d[\text{ClO}_2]}{dt} = -k [\text{ClO}_2][\text{phenol}] \quad (1)$$

in which k = reaction velocity coefficient. The left hand side of the equation is the initial slope and the concentrations are the initial values. Thus k can be readily determined. The conditions of the several experimented runs, the initial slopes and the values of the reaction velocity coefficient are given on Table 4. The relative constancy of k and the lack of any patternal change in the value of k with initial concentrations suggests the assumption of a second-order reaction to be reasonable.

Table 4

Evaluation for Reaction Velocity Coefficient k

<u>Run No.</u>	<u>Initial ClO₂</u> <u>m/l x 10⁴</u>	<u>Initial phenol</u> <u>m/l x 10⁴</u>	<u>pH</u>	<u>Slope</u> <u>x 10⁴</u>	<u>k*</u> <u>1 mole⁻¹ min⁻¹</u>
Buffer conc. = 0.1 molal; ionic str. = 0.3 molal; temp. 22-24°C					
19R	4.35	5.07	3.85-4.15	5.6	2540
20Ar	4.19	5.11	4.02	5.0	2340
21R1	5.88	7.64	3.8	6.7	1490
21R2	5.88	7.64	3.85	6.7	1490
21R3	5.88	7.64	3.75	7	1560
22	5.88	7.85	3.92	5.6	1220
22R	5.88	7.85	3.94	8.1	1760
22R1	5.88	7.85	3.95	12.5	2700
22R2	5.88	7.85	3.94	11.0	2400
22R3	5.88	7.85	3.91	11.0	2400
23	5.24	5.21	3.90	4.2	1538
23R	5.24	5.21	3.93	5.25	1925
23R1	5.24	5.21	3.9	6.02	2205
24	5.52	2.61	3.92	2.18	1513
24R	5.52	2.61	4.00	2.75	1562
24R1	5.52	2.61	3.99	2.54	1763
25	5.24	2.60	3.95	2.14	1571
25R	5.24	2.60	3.95	2.86	2099
25R1	5.24	2.60	3.95	3.06	2246
26	4.75	10.07	3.94	12.32	2576
26R	4.75	10.07	3.95	10.32	2158
26R1	4.75	10.07	3.95	9.68	2024

$$*k = \frac{\text{slope}}{[\text{ClO}_2][\text{phenol}]}$$

Recommendations

The work reported herein establishes procedure that could be used for analyses under a variety of conditions. Attempts should be made to identify reaction products. Runs could be made under a variety of conditions of pH, buffer and temperature. A full scale kinetic and mechanism study is suggested.

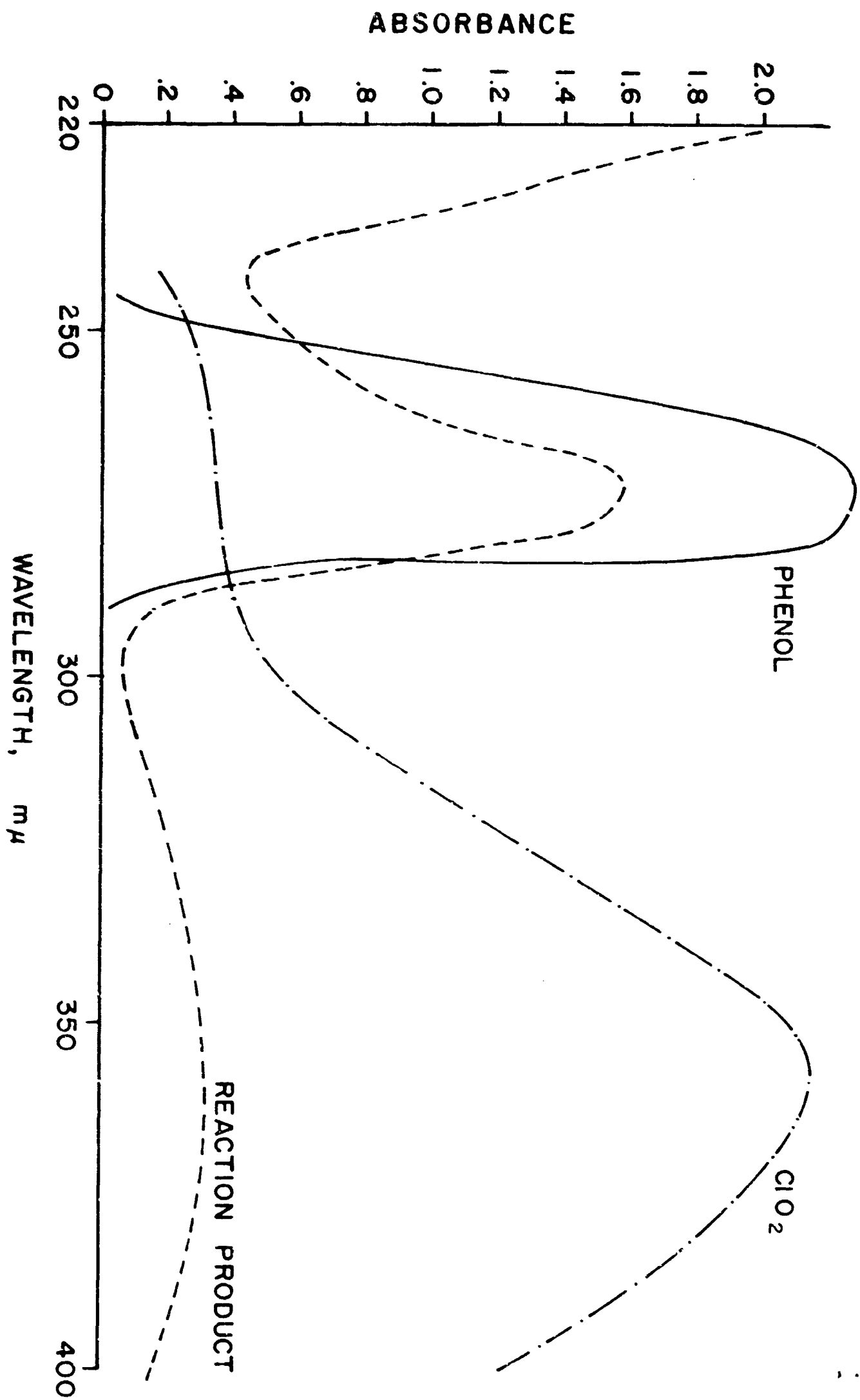


FIG. 1 ABSORPTION SPECTRA OF ClO_2 , PHENOL, REACTION PRODUCT.

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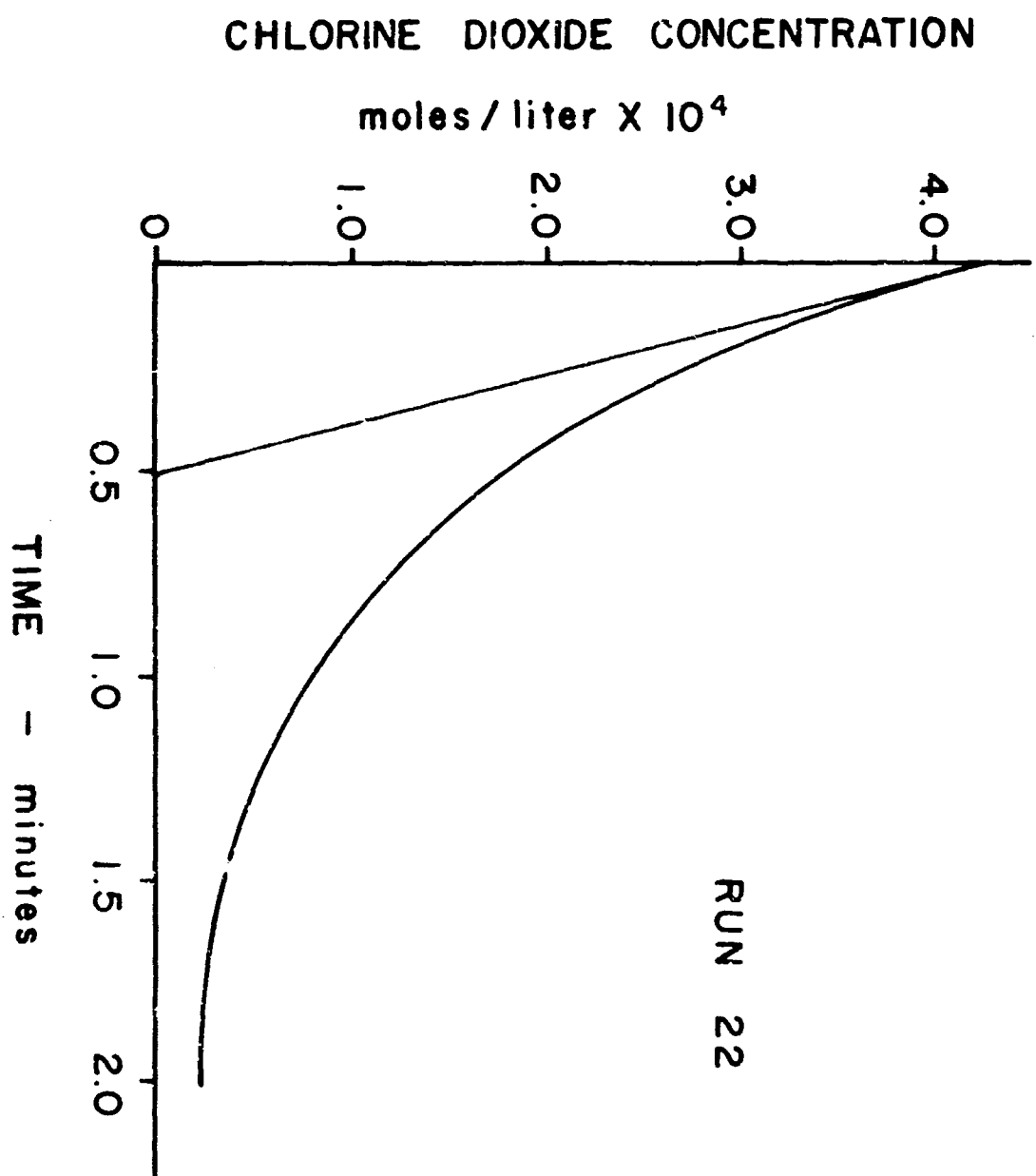


FIG. 2 TRACE OF CHLORINE DIOXIDE WITH TIME